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COMPOUND FOR DRAINING COATINGS  
[COMPOSITION POUR ENROBES DRAINANTS]

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(54) COMPOUND FOR DRAINING COATINGS

(57) Abstract

Asphalt compounds that allow the large-scale use of recycled polyethylene and use of these compounds for the fabrication of draining coatings.

The present invention pertains to asphalt compounds for the preparation of draining coatings. It also pertains to the use of these compounds for the preparation of draining coatings. /2\*

On the majority of roads, traditional bituminous coatings generally provide satisfaction. However, the stresses to which these roads are subject increase from year to year. The axle loads and rolling pressures of tires that are higher and higher and the steady increase of traffic have inevitably an influence on the operating lifetime of these roads. More and more one resorts to bitumens that are modified by polymers and to development of new coating structures in order to combat the harmful effects exerted by these traffic stresses.

The main technical goals looked for in the use of modified bitumens are:

- greater resistance to permanent deformation,
- improved resistance to low temperature fatigue,
- improvement of adhesive and cohesive properties.

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\* Number in the margin indicates pagination in the foreign text.

For many years highway engineering has been trying to use industrial byproducts and, among the latter, recovered plastic materials, that come directly from industry or from household waste, offer a particular benefit from the cost standpoint as well as from the ecological point of view; indeed, this system allows the definitive elimination of waste products and does not present the dangers related to the possible presence of polluting agents in the emission of gases during incineration. To the elastomer modifiers of the SBS type (block co-polymers of styrene-butadiene-styrene) or SBR (rubber styrene-butadiene) and plastomers EVA (ethylene-vinyl acetate) we now add waste from cable manufacturing plants, which are comprised essentially of LDPE (low density polyethylene) mixed with PVC (polyvinyl chloride) and polystyrene, or mixtures of domestic polymers (EP-332245-A).

The draining coatings have been the subject of much interest. They are currently the preferred coating of highways and roads with large amounts of traffic. Their advantages are well known:

- increased safety for users; the avoidance of a film of water on the highway preserves adherence of tires to the ground which ensures a good trajectory and effective braking of the vehicle. The driver is no longer dazzled by multiple reflections of many light sources. The pooling of the water disappears.

- noise reduction: better protection of the environment thanks to an increase of noise absorption properties, in order to reduce the level of perceived noise.
- cost reduction: increased service duration of streamlining and foundation layers thanks to optimal removal of water by the surface draining layer.

The fabrication of draining coatings requires a great deal of care: the compounds that enter into their composition must have particular qualities. The properties are produced by the creation of channels within the thickness of the asphalt, therefore by increasing the volume of voids. From the open structure of coatings, the binder is subject to different constraints from those encountered with traditional bituminous coatings. Therefore, one cannot use the same compounds. In order to effectively fight against these effects and therefore to ensure the durability of draining layers, it is necessary to have a film of binder that is sufficiently thick around each fine gravel piece as well as good binder/granular material adhesiveness. The mechanical cohesion of the coating is obtained traditionally by the addition of new elastomers (SBS) or recycled elastomers (crumbled tires), the goal being to obtain an extremely viscous and elastic binder at service temperatures. The bituminous compounds whose concentration in polyolefin is greater than 5% by weight of bitumen yield binders that are unstable in storage, greatly hardened and having shrinkage phenomena during cooling.

The present invention therefore has the goal of providing an asphalt based compound that has the aforementioned characteristics and that allows the large-scale use of HDPE (high density polyethylene) that has been recycled.

The compounds of the invention are characterized in that they essentially include:

- a mineral skeleton including (by weight)
  - from 79 to 88 parts of ballast with grain size 6/17 (between 6 and 17 mm)
  - from 9 to 15 parts of sand of grain size 0.08/2
  - from 3 to 8 parts of inert ~~filler~~ material with grain size less than 0.08, calculated so as to obtain a total of 100 parts.
- some bitumen having a penetration between 65 and 150 tenths of a mm at 25°C; in quantity corresponding to 3.5 to 7 parts by weight;
- a first modifier chosen in the group that includes the styrene-butadiene or styrene-isooprene co-polymers or a mixture of such co-polymers or recycled tires, in a quantity corresponding to 2 to 7% by weight, calculated for the mass of bitumen, extended possibly from 0 to 3% by weight of oil, calculated with respect to the mass of bitumen.
- a second modifier chosen from the group that includes the

polyolefins, polyethylene terephthalate or a mixture of such polymers, in quantity corresponding to 0.5 to 5 parts by weight, without exceeding the bitumen quantity.

The present invention also has as a goal the use of these compounds for the fabrication of draining coatings.

It pertains in addition to a process for preparation of draining coatings, this procedure being characterized in that one introduces into a mixing unit, at temperatures between 130 and 185°C, preferably about 140°C in industrial application and about 180°C for laboratory scale.

a) a mineral skeleton including:

from 79 to 99 parts of ballast with grain size 6/17

from 9 to 16 parts of sand with grain size 0.08/2

from 3 to 8 parts of inert film material with grain size less than 0.08.

b) or (i) some bitumen having a penetration between 65 and 150 tenths of a mm at 25°C, in quantity corresponding to 3.5 to 7 parts by weight;

(ii) a first modifier chosen among the styrene-butadiene co-polymers, styrene-isoprene co-polymers, recycled tires and their mixtures, in a quantity corresponding to 2 to 7% by weight, calculated with respect to the mass of bitumen, extended possibly from 0 to 3% by weight of oil, calculated with respect to the mass of

bitumen, or 3.57 to 7.7% by weight, calculated for the mineral mass, of a modified bitumen-co-polymer binder (styrene-butadiene or styrene-isoprene or a mixture of such co-polymers) that is homogeneous, prepared in an oven at 150-180°C from the components already described under (i) and (ii).

c) a second modifier chosen in the group including polyolefins, polyethylene terephthalate and the mixtures of such polymers in quantity corresponding to 0.5 to 5 parts, calculated with respect to the mineral mass.

The invention also pertains to the use of rolling surfaces having draining properties, characterized by the previously described compound. The grain size, as used here, must be understood as signified that 80%, and preferably 90%, of the material must have a grain size greater than the lower value and 80%, and preferably 90%, a grain size lower than the upper value.

In a preferred form of implementation, the invention is characterized in that it is comprised of a mixture of about:

- 100 parts of mineral skeleton,,
- 5.1 parts of bitumen,
- 0.2 parts of SBS
- 2 parts of HDPE, preferably recycled.

In a preferred compound the mineral skeleton includes: from 81 to 85 parts of ballast of grain size 7/14 from 11 to 13 parts of sand with grain size 0.08/2

from 4 to 6 parts of fill material with grain size less than 0.08.

The mineral skeleton is characterized by a discontinuous grain size and must have a composition in grain size such that they assure a content of voids in the structure between 15 and 30%, preferably between 15 and 25%.

The ballast must have an increased durability and resistance to polishing. Ballast materials that are used for making such coatings preferably will have the following conditions:

- increased polish coefficient for the fraction  $7/14 > 45\%$   
(NBN B11-204 standard)
- Deval micro coefficient for the category  $10/14 < 10$  (AFNOR NF P18-572 standard of October 1978)
- Los Angeles coefficient for category  $10/14 < 15$  (AFNOR NF P18573 standard of October 1978).

The ballast must be chosen from among the traditional materials such as flint, porphyry, quartzite, grit, for example.

The fill material can be chosen from among the fines of inert materials with grain size less than 0.08, such as for example cement, crushed stones fines, fly ash, clay powder or other materials.

The bitumens are present at the rate of 3.5 to 7 parts. The bitumens that can be used for making such coatings are bitumens for highway use, preferably distillation bitumens or reconstituted bitumens having penetration values between 65 and 150 dmm (according

to the ASTM D-5 or IP 49 standard) and Ring and Ball values between 40 and 59°C (ASTM D-36 or IP 58). These bitumens can possibly be acidified and/or given antioxidants. The preferred qualities of bitumen have penetrations between 80 and 100 dmm.

The compound includes an addition from 2 to 7% by weight with respect to the bitumen (preferably 4 to 7) of a butadiene-styrene elastomer. As the particularly appropriate co-polymer, we can mention the co-polymers of the type SBR, SBS linear or radial. Also usable are the styrene isoprene co-polymers, for example SIS (block styrene-isoprene-styrene copolymers). These elastomers can be used in new or recycled form, alone or in a mixture, extended or not with 0 to 3% oil (oil introduced during the preparation of the SBS or oil incorporated during the use of the recycled SBS in the form of a rubber powder). /4

The compound finally includes from 0.5 to 5 parts by weights, preferably 0.5 to 3, with respect to the mineral mass of a polyolefin or polyethylene terephthalate, alone or in a mixture, new or recycled. The polyolefin will be chosen preferably among products resulting from the polymerization or the co-polymerization of ethylene or propylene, for example polyethylene (high or low density), polypropylene or co-polymers of ethylene-propylene-diene that are monomeric. More particularly, during the use of HDPE the quantities will preferably be limited to 0.5 to 3 parts by weight.

The invention also allows one to recycle dry containers after crushing. The damp containers of aqueous or oily solutions (up to 30% by weight of the container) can also be used, without prior washing. The preferred recycled product is present in the form of pieces of shredded HDPE.

In general a draining coating can be prepared according to two different methods:

a) mixing of ballast with premodified binder; this type of preparation presents the problem of homogeneity of the binder that must be prepared freshly and constantly stirred in order to avoid decantation, and does not allow one to incorporate large quantities of polyolefins.

b) extemporaneous preparation of the compound for draining coating; this type of preparation, which is the aim of the invention, has the advantage of preventing problems of decantation during storage and allows one to incorporate significant quantities of polyolefins so that one can pre-measure the second modifier. The order of addition of the different elements of the compound is not important. The composition according to the invention in particular has the following advantageous properties:

increased Marshall stability

certain ecological impact: recycling of significant quantities of polyolefins.

The direct addition of HDPE to the asphalt allows maximum recycling of 3% with respect to the mass of the asphalt, which represents 20 times the maximum usable quantity via the modified bitumen. The following examples are given by way of illustration of the present invention and do not include any limiting nature. The Marshall test characterizes the properties of mechanical resistance (stability) and plastic resistance (flowing) but does not allow one to validly measure all of the mechanical properties of the draining asphalt. Only the measurements of stability are significant comparable.

Examples:

All of the experiments were conducted under the same operating conditions. The mineral aggregates were strained on appropriate sieves or screens in order to obtain the necessary calibers and to eliminate fine adhering particles (wet screening). The mineral aggregates were dried in an oven at 105-110°C, according to caliber, up to a constant mass.

Individually, by beginning with the fill material, we cumulatively weigh with precision of 0.5 g the quantities of required materials (in increasing nominal calibers). The aggregate is then mixed and brought into the oven at a temperature of 185°C.

The quantity of binder to be used (2 kg) is brought to 180°C and introduced with precision of 0.1 g in the pre-heated mixing receptacle to the mixing temperature (170°C).

Next one adds the cold HDPE and the hot aggregate. The material is perfectly mixed as quickly as possible (135 sec maximum) to obtain a mixture in which the bitumen is regularly distributed.

Example 1:

The tested coating has the following composition:

1) mineral skeleton (meeting the conditions described earlier)

Bande crushed stone 7/14: 82 parts

Bande crushed stone 0/2: 14 parts (including 1 part of fines)

Ankersmit type fines 1: 4 parts

2) 5.1 parts by weight of bitumen 80/100.

3) 0.2 parts by weight of Finaprene (trademark deposited by Petrofina) 401 powder (styrene-butadiene-styrene copolymer; 22% styrene)

4) second modifying agent: 1 part by way of dry HDPE.

Example 2:

Compound identical to example 1 for the mineral skeleton, bitumen and the first modifying agent, but with the addition of 2 parts by way of dry HDPE.

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Example 3:

Compound identical to example 1 for the mineral skeleton, the bitumen and the modifying first agent, but addition of one part by weight of oily HDPE (oil content 26.1% with respect to the HDPE).

Example 4:

Composition identical to example 3 for the mineral skeleton, bitumen and the first modifying agent, but with the addition of two parts of oily HDPE.

Comparative example A:

The tested coating has the following composition:

- 1) mineral skeleton: identical to example 1.
- 2) 5.3 parts by weight of bitumen 80/100.

There is no modifying agent.

Comparative example B:

Composition identical to example 1 for the mineral skeleton, bitumen and first modifying agent, but no addition of second modifying agent.

Comparative example C:

Composition identical to example 1 for the mineral skeleton, bitumen and the first modifying agent, but with the addition of 0.3 parts by way of cellulose as the second modifying agent.

Comparative example D:

The testing coating has the following composition:

- 1) mineral skeleton: identical to example 1.
- 2) 5.3 parts by weight of modified bitumen comprised of 91% bitumen 80/100, 6% of Finaprene (trademark deposited by Petrofina) 480 styrene-butadiene-styrene copolymer; 30% styrene; oil content: 50 parts per 100 parts of rubber) and 3% HDPE.

The quantities and the results are summarized in the following table in which:

AD: direct addition of SBS and modifying agent to the coating

PM: binder prepared with the coating (pre=mix)

(\*): oil content: 26.1%

401P: Finaprene 401 powder 480: Finaprene 480

From reading the results of table 1 one can determine that the resulting coatings according to the invention have better properties of use.

TABLE 1: Marshall Tests on Draining Components

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	Procedure	Binder	First modifying agent	Second modifying agent	Void	Stability (kN)
EX 1	AD	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 parts	HDPE dry 1 part	21.78	6.20
EX 2	AD	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 parts	HDPE dry 2 parts	20.80	8.65
EX 3	AD	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 parts	HDPE oily 1 part (*)	21.78	5.10
EX 4	AD	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 parts	HDPE oily 2 parts (*)	19.60	5.55
EX A	PM	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 parts	....	21.72	3.40
EX B	AD	Bit 80/100 5.1 parts	Finaprene 401P 0.2 parts	....	22.22	4.80
EX C	AD	Bit. 80/100 5.1 parts	Finaprene 401P 0.2 part	Cellulose 0.3 parts	20.55	4.50
EX D	PM	Modified bitumen 5.3 parts (91% bit. 80/100; 6% Finaprene 480; 3% HDPE)			21.84	4.25

1. Compounds based on asphalt that essentially include:

- the mineral skeleton including (by weight) from 79 to 88 parts of ballast with grain 6/17 from 9 to 15 parts of sand with grain size 0.08/2 from 3 to 8 parts of inert fill material with grain size less than 0.08, calculated to obtain a total of 100 parts.
- some bitumen having a penetration between 65 and 150 tenths of a millimeter at 25°C; in quantity corresponding to 3.5 to 7 parts, calculated for the mineral mass;
- a first modifier chosen in the group including the styrene-butadiene or styrene-isoprene co-polymers or a mixture of such co-polymers or recycled tires, in a quantity corresponding to 2 to 7% by weight calculated for the mass of bitumen, possibly extended from 0 to 3% by weight with oil.
- a second modifier chosen in the group including the polyolefins, polyethylene terephthalate or a mixture of such polymers, in quantity corresponding to 0.5 to 5 parts, calculated for the mineral mass.

2. Compounds according to Claim 1 in which the mineral skeleton includes:

from 81 to 85 parts of ballast with grain size 7/14

from 11 to 13 parts of sand with grain size 0.08/2  
from 4 to 6 parts of fill material with grain size less than  
0.08.

3. Compounds according to Claims 1 or 2 characterized in that the bitumen has a penetration between 80 and 100 tenths of a millimeter.

4. Compounds according to Claims 1 to 3 in which the first modifier is introduced in a quantity corresponding to 4 to 7% by weight.

5. Compounds according to Claims 1 to 4 in which the second modifier is introduced in quantity corresponding to 0.5 to 3 parts by weight.

6. Use of compounds according to Claims 1 to 5 for the fabrication of draining coatings.

7. Procedure for preparation of compounds according to any of the Claims 1 to 5 characterized in that one introduces into a mixing unit at temperatures between 130 and 185°C.

a) the minerals skeleton,  
b) the bitumen and the first modifier possibly extended by oil or the modified bitumen-co-polymer homogeneous binder previously mixed in a container at 150-180°C,  
c) the second modifier.

8. Procedure for preparation according to Claim 7 in which the components are introduced into the mixing unit a temperature of about 140°C.

9. Rolling surfaces having draining properties, characterized by the compositions according to any one of the Claims 1 to 5.